Mechanisms for hetero-epitaxial nucleation of $YBa_2Cu_3O_{\sim 6.1}$ at the buried precursor/$SrTiO_3$ interface in the postdeposition reaction process

L. Wu, V. F. Solovyov, H. J. Wiesmann, Y. Zhu, and M. Suenaga[a]

Materials and Chemical Science Division, Energy Sciences and Technology Department,
Brookhaven National Laboratory, Upton, New York, 11973

The mechanisms have been identified for the hetero-epitaxial nucleation of $YBa_2Cu_3O_{\sim 6.1}$ (YBCO) at the buried interface between a precursor film and $SrTiO_3$ for the so-called BaF_2 process which is a postdeposition reaction process for the synthesis of epitaxial YBCO films. It is shown that the preferential nucleation of YBCO at the interface is due to (1) the strong chemical affinity of the (Y, Ba)-oxy-fluoride, an intermediate phase, to $SrTiO_3$ and (2) the epitaxial alignment of its (111) planes with the (001) surface of the $SrTiO_3$ which reduces the activation barrier for the formation of YBCO. In thin films ($<2-3$ μm) the YBCO nuclei, whose c axes are perpendicular to the $SrTiO_3$ surface, form directly from this aligned oxy-fluoride. In thick films (5 μm), however, this oxy-fluoride decomposes into a disordered transitory cubic phase which then orders to form YBCO nuclei with three orientational variants, one with its c axis perpendicular and two with their c axes parallel to the (001) plane of $SrTiO_3$. © *2002 American Institute of Physics.*
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The successful growth of the biaxially aligned thick films of $YBa_2Cu_3O_7$ (YBCO), a high-critical-temperature superconductor, on a flexible metallic substrate is essential to its use for electric power devices as well as high-field magnets operated at elevated temperatures. The so-called BaF_2 process, a postdeposition reaction process, is considered to be one of the most promising methods for the fabrication of such tapes. In this process, precursor films are deposited onto an oxide substrate or a metallic tape with an oxide buffer layer, and heated to form YBCO in an atmosphere of a flowing process gas, N_2, O_2, and H_2O. The precursor deposition methods can be an electron-beam (e-beam) evaporation method,[1–3] or by a sol–gel process using tri-fluoroacetates.[4,5] The precursor film consists of fine ($\sim$10 nm) grains of Y, Cu, and BaF_2 when it is deposited by e-beam evaporation. Upon heating, it quickly turns to a mixture of Cu_2O and a (Y, Ba) oxy-fluoride, and then from this mixture the c-axis-oriented YBCO is grown on a substrate as the oxy-fluoride decomposes, reacting with H_2O in the process gas. The mechanism for the growth of YBCO layers is shown to be the homo-epitaxial precipitation of YBCO onto the existing c-axis-oriented YBCO layer from a thin liquid layer containing Y, Ba, Cu, and O.[6] The Y–Ba oxy-fluoride, whose approximate composition is $(Y_{0.3}Ba_{0.7})(O_{0.15}F_{0.85})_2$, decomposes at its interface with the liquid releasing HF to the process gas. The decomposition of this phase and CuO provides the necessary cations and oxygen to the liquid. Also, the basic growth-rate-limiting process is known to be the removal rate of the reaction product HF from the surface of the film into the processing atmosphere.[7] Hence, the general process for the YBCO growth in the BaF_2 process is well understood. However, the nucleation process(es) of YBCO at the substrate surface, particularly the effect of the precursor thickness on the crystallographic orientation of the nuclei, is not yet understood.

Understanding of this nucleation process is particularly important for the fabrication of technologically viable thick YBCO film conductors. This is because the growth of the non-c axis YBCO becomes prevalent as the thickness of the films increase beyond $2-3$ μm, and is very detrimental to keeping high values of superconducting critical current density J_C. The required thickness for most applications is considered to be $\sim$5 μm or greater. Here, we will present the results of our recent study toward the clarification of the mechanisms of the YBCO nucleation in the BaF_2 process using precursor films which were deposited by e-beam evaporation. Transmission electron microscopy (TEM) and x-ray diffraction (XRD) techniques were employed for the study.

As described previously, the stoichiometric precursor films were co-deposited by e-beam evaporation of Y, Cu, and BaF_2.[8] Substrates were 3 mm$\times$10 mm$\times$0.5 mm polished [001] $SrTiO_3$ (STO). YBCO synthesis was performed in a 50-mm-diameter quartz tube in a tube furnace. The flowing process gas consisted of a mixture of 100 mTorr of O_2 and 25 Torr of H_2O in N_2 at atmospheric pressure. The gas-flow rate and the temperature were kept at 0.2 l/min and 735 °C, respectively. In order to study the nucleation process for YBCO, several specimens with different film thickness (1, 3, and 5 μm) were heated and quickly pulled out of the tube after the prescribed heat treatment times, 10, 20, 30, and 40 min. Here, for brevity, the examination of 1 and 5 μm thick films are primarily discussed and the work on 3 μm thick films are reported elsewhere.[6] All specimens were studied by XRD for the overall phase development, while TEM techniques were used for selected specimens for a detailed examination of the microstructural and the phase evolution of the films. TEM was performed on the cross sectioned films using JEOL-3000F equipped with a windowless energy-dispersive and an electron-energy-loss spectrometer.

The morphology and phase composition of the precursor
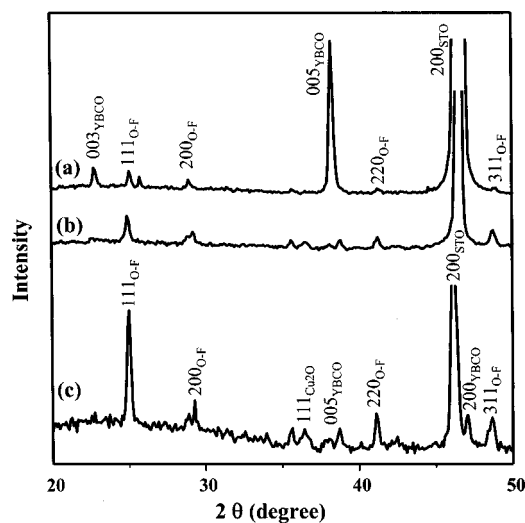
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[a]Electronic mail: mas@bnl.gov

FIG. 1. Intensities as a function of angle for XRD measurements from the quenched precursor films are shown. (a) 1-μm and (b) 5-μm-thick film after 20 min, and (c) 5-μm-thick film after 30 min. For brevity, only the major lines are identified.

FIG. 2. (a) High-resolution image of the region from a 1-μm-thick film heated at 735 °C for 20 min showing YBCO and the oxy-fluoride on STO. These phases have epitaxial relationships characterized by (001)YBCO$\|(001)$STO, (110)YBCO$\|(110)$STO. (b) and (c) The electron diffraction patterns from the ordered (Y, Ba)-oxy-fluorides showing two types of the ordering O_1 and O_2, respectively.

evolved quickly with annealing times. After 10 min at 735 °C, the precursor consisted of Cu_2O and a Y–Ba oxy-fluoride (cubic, $a = 0.618$).[6] As observed earlier, the oxy-fluoride had a strong tendency to align epitaxially its (111) plane parallel to the (001) plane of STO adjacent to the substrate, but there was no clear indication of YBCO nucleation yet. Further heat treatments of the films revealed that the heat-treatment duration required for the nucleation of YBCO was dependent on the thickness of the films. After 20 min, c-axis oriented YBCO was observed by XRD in a 1-μm-thick film, but it was absent from 3- and 5-μm thick films. The XRD patterns for 1- and 5-μm thick films are shown in Figs. 1(a) and 1(b). For 5-μm-thick films, there were weak indications of YBCO formation in the XRD from the specimen which was heated for 30 min as indicated by weak $(h00)$ and $(00l)$ lines in Fig. 1(c) and, as discussed next, some nuclei of YBCO were also found by TEM in the specimen. It took an additional 10 min of heating before there was a clear indication of YBCO in XRD and the strongest lines in this film were $(h00)$ lines indicating the growth of a substantial non-c-axis-oriented YBCO. (For convenience, we will call these $(h00)$ nuclei as the a-axis YBCO.) Also, XRD lines, not belonging to YBCO, were identified with those of Cu_2O, the disordered and the ordered (Y, Ba) oxy-fluoride phases which are discussed next.

In the cross sectional TEM images, the thin ($\sim$60 nm) c-axis aligned YBCO layer was observed in the 1-μm-thick film specimen along the surface of the substrate. These covered nearly the entire surface after being heated for 20 min. The remaining areas were occupied by the epitaxially aligned (111) plane of the oxy-fluoride as exhibited in Fig. 2(a) which shows the alignment of the (001) planes of YBCO and the (111) planes of the oxy-fluoride with the (001) plane of the STO. These and the earlier observation of the propensity for the alignment of the (111) plane of the oxy-fluoride to the (001) surface of the STO suggest the mechanism for the preferential nucleation of the YBCO only at the STO surface while the composition of the film is the same throughout. Since the YBCO formation does not take
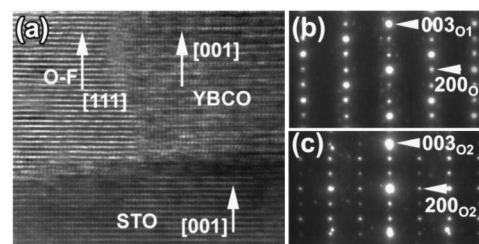
place from the precursor mixture alone, the alignment of the oxy-fluoride appears to lower the activation energy for the formation at the precursor/STO interface, and allows the nucleation of YBCO only at the interface.

Previously, we reported the possibility that the Y–Ba oxy-fluoride orders along its [111] direction at the precursor/STO interface region in 3-μm-thick films. The periodicity of the ordered structure was three times its disordered (111) spacing, and was nearly identical to that for the (001) spacing of YBCO. Thus, we speculated that this ordering played a role in the nucleation process of YBCO.[6] In 5-μm-thick films, we observed clear indications of such ordering taking place. In fact, two distinguishable ordered structures were observed in these thick films which were heated for 20 and 30 min. Electron diffraction patterns of the ordered oxy-fluoride from a 5-μm film heated for 20 min are shown in Figs. 2(b) and 2(c). One of the ordered structures O_1 [Fig. 2(b)] is a tetragonal with $a = 0.757$ and $c = 1.07$ nm. The other O_2 [Fig. 2(c)] is an orthorhombic with $a = 1.063$, $b = 1.078$, and $c = 1.07$ nm. The crystal-structural relationships between the disordered oxy-fluoride and the ordered oxy-fluorides are as follows: $d_{O_1}^{001} \sim d_{O_2}^{001} \sim 3d_{O-F}^{111}$, $d_{O_1}^{100} \sim 1/\sqrt{2}d_{O_2}^{100} \sim 3d_{O-F}^{211}$, and $(001)_{O_1,O_2}\|(111)_{O-F}$, where subscripts O_1, O_2, and O–F represent ordered tetragonal and orthorhombic, and disordered oxy-fluorides, respectively. All of these oxy-fluoride phases have also epitaxial relationships with STO.

In the 5-μm-thick specimen, which was heated for 30 min, YBCO nuclei, and on rare occasions, a new transitory phase (for convenience, we denote this as the T phase) were found at the STO surface in addition to small Y_2O_3 precipitates, and the disordered and the ordered oxy-fluorides. In contrast to the 1-μm-thick film, the YBCO nuclei were oriented not only with its c-axis perpendicular, but also parallel to the (001) plane of the STO. The lateral sizes of the YBCO nuclei were 50–150 nm, and their compositions varied, but the average was the same as those found in the 1-μm-thick film which was heated for 20 min., i.e., $YBa_2Cu_{1.5-2.0}O_x$. The T phase was a cubic phase and contained Y, Ba, Cu, and O, but not F. This is shown in Fig. 3(a). Its composition was similar to that of YBCO nuclei, and its basic planes were parallel to the corresponding basic planes of STO. The d spacing for its (001) plane was 0.393 nm, which was larger than that of the (111) spacing of the disordered oxy-fluoride (0.357 nm), and was very close to one third of the d spacing
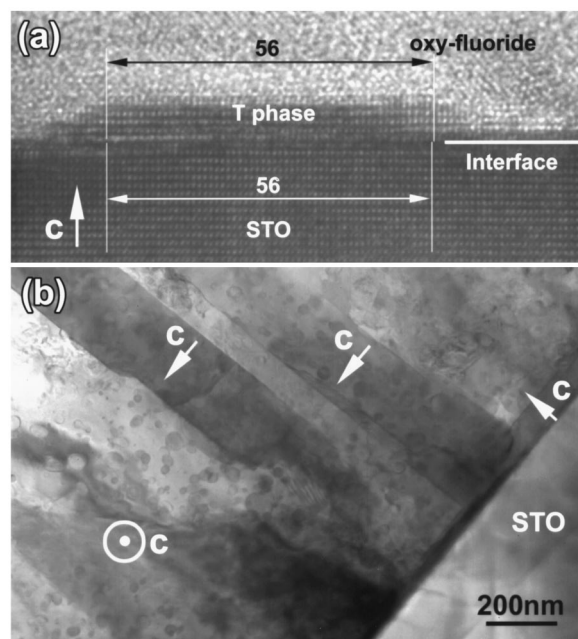
FIG. 3. (a) High-resolution image of the transitory T phase on STO and (b) a low-magnification image of an area where the YBCO grains with three orientational variants in a 5-μm-thick film.

of the (001) plane of the YBCO (1.168 nm). This phase appeared to be formed by the replacement of F by Cu and O in the aligned oxy-fluoride, and we believe that it was a transitory phase before it is ordered to form the YBCO nuclei from the oxy-fluoride and Cu$_2$O. More importantly, this phase appears to assist in the formation of the *a* axis as well the *c*-axis-oriented YBCO nuclei when it orders to form YBCO. This is because the T phase is a disordered cubic phase, and this will allow the formation of the YBCO nuclei in three orientational variants, i.e., two *a*-axis and one *c*-axis orientations, when it orders tetragonally to form YBCO. (Note that a disordered cubic YBCO, which is similar to the aforementioned proposed T phase, has been reported in the films which were deposited by pulsed laser deposition techniques).[9] In order to confirm these orientational variants of the YBCO growth, we examined the relative orientations of the substantially grown YBCO in a specimen similar to one which was heated for 40 min. A low-magnification TEM image from it is shown in Fig. 3(b) where the *a*-axis and the *c*-axis growth are clearly observed. As a confirmation of this supposition of the role of the T phase in the nucleation of the *a*- and *c*-axis-oriented YBCO grains, we found the three variants in the relative orientations for YBCO grains, i.e., the *c*-axis, and two *a*-axis grains as indicated in Fig. 3(b). Note that two *a*-axis grains are mutually perpendicular to each other.

One can speculate the difference(s) between 1- and 5-μm-thick films leading to the difference in the orientations of the nuclei. It is possible that the formation of the ordered oxy-fluoride in thick films may assist the formation of the T phase since the ordered phase was not observed at all in 1-μm-thick films and was less in 3-μm than in 5-μm-thick films. Further, this may be allowed by the limited diffusivity of H$_2$O and HF in thicker films, which delays the formation of the nuclei and provides the extended time required for the formation of the ordered phases. Since the growth rate for the *a*-axis grains is so much greater than that for the *c*-axis one, these become prevalent as the films become thicker (>2–3 μm) and/or the growth rates are increased ($\geqslant 0.1$ nm/s) and hence very low values of J_C. Thus, finding the means to prevent this type of the growth is extremely important for the successful fabrication of the commercially viable YBCO conductors.

In summary, it has been shown that the preferential nucleation of the *c*-axis-oriented YBCO at the precursor/substrate interface, but not in any other parts of the film, was due to the lowering of the activation energy for the formation via the hetero-epitaxial alignment of the (111) plane of the (Y, Ba)-oxy-fluoride onto the (001) surface of the STO. In thick films, the *a*-axis-oriented YBCO nucleated through the formation of the transitory cubic phase and these grew rapidly to exhibit strong intensities for the (h00) lines in XRD. The formation of a cubic transitory phase allowed the formation of three orientationally variant nuclei as it crystallographically orders to form the tetragonal YBCO. Furthermore, the formation of the transitory phase is possibly promoted by the formation of the $\langle 111 \rangle$ ordered oxy-fluoride in thick films. However, in order to confirm this possibility it requires a further investigation.

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